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Application of C_{18} disks followed by gas chromatography techniques to degradation kinetics, stability and monitoring of endosulfan in water

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Abstract

A comparative degradation study of endosulfan spiked at 35 μg/l in water using photocatalysis with ($FeCl_3/H_2O_2$)/(TiO_2/H_2O_2) and photolysis using either a xenon arc lamp and/or sunlight was performed. After irradiation the water samples were preconcentrated using C_{18} solid-phase disk extraction and analysis by gas chromatography–electron capture and mass spectrometric detection. Endosulfan sulphate was found in the photodegradation studies. Endosulfan showed high stability in water when it was exposed to sunlight and xenon arc lamp, but by means of photocatalysis with $FeCl_3/H_2O_2$, TiO_2/H_2O_2, the degradation was very fast with half lives varying from 59–98 min. The degradation kinetics followed a first order reaction and the R.S.D. of rate constants, for $n=3$, varied from 4–17%. The stability of endosulfan on C_{18} Empore disks has been determined at 20°C, 4°C and −20°C for periods up to 3 months. Endosulfan was not degraded on C_{18} Empore disks. Ground water samples from south of Spain (Almeria) were monitored during 1 year. The compounds α-, β- and endosulfan sulphate were detected at concentration values varying from 0.5–540 ng/l.

Keywords: Kinetic studies; Environmental analysis; Water analysis; Endosulfan; Pesticides; Organochlorine compounds

1. Introduction

Endosulfan is a mixture of two stereoisomers, α and β, and registered with several trade marks, Thiodan, Cyclodan, Thimol, Thiofar and Malix. Endosulfan is a popular organochlorine insecticide because of its favorable toxicological action and low persistence in comparison with other organochlorine insecticides [1].

Several hundred pesticides of different chemical composition are currently widely used for agricultural purposes throughout the world. Data on the environmental fate of pesticides are required in order to determine the potential of a pesticide to reach groundwater including information on its hydrolysis, photolysis, aquatic metabolism, leaching and field dissipation [2]. In this respect, we reported the degradation of various pesticides in water under natural sunlight and xenon arc lamp [3–6]. The degradation of endosulfan in water is a complex process and depends upon the type of water, microorganisms, pH and oxygen content of the water [7].

Different studies on endosulfan degradation have been reported in the literature. Putman et al. [8] found the maximum loss of total endosulfan and related residues calculated as endosulfan at 7 days when endosulfan residues on alfalfa were exposed to drying by sunlight and air. No endosulfan lactone was detected. Donald [9] showed that α-endosulfan decomposed fairly rapidly (50% in 60 days) and β-endosulfan slowly (50% in 800 days) in soil. Archer et al. [10] found diol as a major product

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along with α-hydroxyether, lactone and ether of endosulfan, after irradiation with UV light. Miles and Moy [11] found that α-endosulfan was converted to greater extent than β-endosulfan and both converted primarily to endosulfan diol. Dureja et al. [12] irradiated α- and β-endosulfan in triethylamine with UV light above 300 nm and sunlight and monodechlorinated products were formed by loss of one chlorine atom. Walker et al. [13] found that endosulfan disappeared faster as a result of the presence of formalin. Cotham and Bidleman [14] determined half-lives of endosulfan in unsterile seawater at pH 8.0, being 4.9 days for the α-isomer and 2.2 days for the β-isomer; in seawater/sediment system at pH 7.3–7.7, the half-lives were 22 days for the α-isomer and 8.3 days for the β-isomer. Endosulfandiol was identified as a degradation product of endosulfan. Various studies agreed about the faster degradation of α-endosulfan versus β-endosulfan [15–20].

Since no photocatalysis study of endosulfan with TiO_2/H_2O_2 and $FeCl_3/H_2O_2$ were carried out up till now, we decided to carry out this study. Photocatalytic oxidation by semiconductor oxides such as TiO_2 or the Fenton reagent is an area of environmental interest for the treatment of contaminated wastewaters [21]. In previous papers, we have reported [6,22] the degradation of two other pesticides, alachlor and chlorpyrifos, and good results were found because of the photocatalytic process degraded these pesticides very quickly, $t_{1/2}$ 10–17 min for alachlor and 15–27 min for chlorpyrifos.

Since endosulfan is used in greenhouses in Almeria (South of Spain), we decided to undertake a monitoring program in groundwater, following our previous monitoring of carbamates in the same region [23]. In addition, all water samples were transported from Almeria to Barcelona (1000 km) so a stability study of endosulfan after preconcentration on C_{18} disks was carried out, using methodology of our previous works on the stability of pesticides in water samples [24,25].

The objectives of this study were (1) to compare the degradation kinetics of α- and β-endosulfan in water by using natural photolysis, xenon arc irradiation, photocatalysis with TiO_2/H_2O_2 and $FeCl_3/H_2O_2$ (2) to study the stability of α- and β-endosulfan on C_{18} SPE disks at 20°C, 4°C and −20°C during a period of 3 months (3) to determine the degradation products by means of GC–ECD and GC–MS and (4) to carry out the monitoring of α-, β- and endosulfan sulphate in the ground waters of Almeria.

2. Experimental

2.1. Chemicals

α-Endosulfan (98%), β-endosulfan (98%) and endosulfan sulphate (98%) were from Chem Service (Tower Lane, USA), iron(III) chloride 6-hydrate (98–102%) from Panreac (Barcelona, Spain) and titanium dioxide P25 from Degussa (Japan). Ethyl acetate was obtained from Panreac, methanol and acetone were purchased from Merck (Darmstadt, Germany). Hydrogen peroxide (30% solution) was from Foret (Barcelona). Organic-free water (pH 8.0) was prepared with a Milli-Q system from Millipore-Waters. Ground water (pH 6.85, 465 mg/l of sulphates, 183 mg/l of chlorides, 1058 mg/l of anions, 146 mg/l of Ca, 186 mg/l of Mg, 470 mg/l cations and conductivity 2000 μS/cm) was used in some of the experiments. Empore 3M, extraction disks C_{18} were from J.T. Baker (Deventer, Netherlands).

2.2. Chromatographic conditions

The kinetics of photodegradation, study of stability and monitoring was determined by gas chromatography using a Hewlett-Packard 5890 equipped with an electron-capture detector. A DB-5 column (30 m×0.23 mm I.D.) was programmed from 60–300°C at 6°C/min; 60°C was held for 1 min and 300°C was held for 5 min. Injector and detector temperatures were 270°C and 310°C, respectively. Helium was used as the carrier gas at 2.8 ml/min and was used as the make-up gas at 70.0 ml/min.

2.3. Mass spectrometric analysis

A Fisons MD 800 mass spectrometer coupled to a Fisons GC 8000 apparatus was used for GC–MS in the electron impact (EI) mode. EI spectra were obtained at 70 eV, in full scan mode from m/z 50 to 500. A HP-5 column (30 m×0.25 mm I.D.) was programmed from 60 to 300°C at 6°C/min; 60°C

was held for 1 min and 300°C was held for 5 min. Injector and detector temperatures were 270°C, ion source temperature 280°C. Helium was used as the carrier gas with a pressure of column head of 12 p.s.i. (1 p.s.i.=6894.76 Pa).

2.4. Photodegradation experiments

Irradiations were carried out using a Suntest apparatus from Heraus (Hanau, Germany) equipped with a xenon arc lamp, as reported previously [5].

Others experiments were carried out using natural sunlight irradiation, with quartz reservoirs placed capped on a terrace roof from our institute in Barcelona, during August 1996. Water samples, spiked with α- and β-endosulfan by adding the standard pesticide in ethyl acetate, were placed in quartz reservoir of 500 or 1000 ml. Endosulfan concentration in water for the kinetic studies and identification of degradation products was 35 μg/l. At different periods of time, water samples were removed from the reactor and stored at 4°C. The preconcentrated volume of water was of 25 and 50 ml.

2.5. Photocatalysis experiments

Irradiations were carried out using a Suntest apparatus and natural sunlight irradiation. Water samples, spiked with α- and β-endosulfan by adding the standard pesticide in ethyl acetate, were placed in quartz reservoir of 500 or 1000 ml. The endosulfan concentration in water for the kinetic studies and identification of degradation products was 35 μg/l. At different periods of time, water samples were removed from reactor and store in refrigerator. The preconcentrated volume of water was of 25 and 50 ml.

In the experiments $FeCl_3$ or TiO_2 were used, at concentrations of 15 mg/l (as Fe^{3+}) and 10 mg/l (as TiO_2), respectively. In all experiments, H_2O_2 at 0.05% (v/v) was added. The experiments began with the addition of either TiO_2 or $FeCl_3$ to the water, then the mixture was homogenized for 15 min by careful agitation followed by the addition of endosulfan standard solution, followed by agitation and finally the was H_2O_2 added.

2.6. Recovery on C_{18} empore disks

The recovery of endosulfan isomers was done at two concentrations. The first was approximately the concentration of photodegradation experiments (35 μg/l) and the second was half the concentration of photodegradation experiments (17.5 μg/l). The recovery of endosulfan sulphate was done at similar concentrations. The volume used in preconcentration on C_{18} Empore disks varied between 25 and 800 ml.

2.7. Stability on C_{18} empore disks

The stability of α- and β-endosulfan was carried out at three temperatures, −20°C, 4°C and 20°C, during 3 months and in triplicate. The volume used in preconcentration on C_{18} disks was 50 ml, and the concentration was 17.5 μg/l.

2.8. Sample preparation

The water sample removed from reactor was preconcentrated and the procedure followed previous work from our laboratory [4,5]. A C_{18} Empore disk was placed on a sintered glass filter funnel apparatus attached to a vacuum source. A 10-ml volume of ethyl acetate were added to the filter funnel and the disk was dried for 2 min. Subsequently, 10 ml of acetone were added and the disk was dried for 5 min. Then 15 ml of methanol were added and after almost all the methanol was drawn through the disk, 10+10 ml of deionized water were added. When the deionized water was almost drawn through the disk, 25 or 50 ml of water sample were added. The vacuum was then left on for 30 min to allow the disk to dry. The filtration system was put in a reservoir to receive the extract of endosulfan isomers and the degradation products. The extraction was done with three 20-ml portions of ethyl acetate. When the first portion was added, the vacuum was left on for on 5 min and when the second and third portions was added, the vacuum was left for 3 min. The solvents and sample were drawn through the disk at a rate of approximately 0.5 ml/s. The reservoir with the extract was placed in a rotaevaporator system and the extract was carried to a volume between 0.1 and 1.0 ml, depending of the analysis (GC–ECD or GC–MS) and the

preconcentrated water sample. The concentrated extract was analyzed by GC–ECD or GC–MS. The samples were quantified by external standard using automated injection. Calibration graphs in GC–ECD were performed by plotting area (Y) versus amount injected (X), with the calibration equation constructed at absolute amounts of endosulfan isomers injected of 6, 11, 27, 82, 136, 273, 546, 819, 1091 and 1364 pg for the α-isomer and 4, 9, 22, 67, 111, 222, 444, 666, 888 and 1110 pg for the β-isomer. The calibration was done each day of analysis, and R^2 varied between 0.990 and 0.999 for α-isomer, and 0.993–0.999 for β-isomer.

2.9. Calculation of half-life

The calculation of the half-life [26] was performed using the first-order rate equation:

$$C_t = C_0 e^{-kt} \quad (1)$$

where C_t represents the concentration at time t; C_0 represents the initial concentration; and k is the rate constant. When the concentration is reduced to 50% of its initial amount, half-life ($t_{1/2}$) can be determined by:

$$t_{1/2} = 0.693/k \quad (2)$$

where k is the degradation constant.

3. Results and discussion

3.1. Recovery studies

For recovery studies (Table 1) the same concentration used in the photodegradation experiments was used and high recoveries at low volume of preconcentration, 25 and 50 ml were found. For this reason, we removed between 25 and 50 ml from reservoir of the sample after photodegradation. Moreover, we used another concentration in recovery experiments, the half of concentration of photodegradation experiments, because it reflects better the photodegradation reaction. The recovery is slightly better at low concentration (Table 1). For the concentration and volumes of preconcentration used in the photodegradation experiments, the recoveries were 72.97% for the α-isomer at 25 ml and 34.72 μg/l, 84.95% for α-isomer at 50 ml and 34.72 μg/l, 84.02% for β-isomer at 25 ml and 34.10 μg/l, and 78.06% for β-isomer at 50 ml and 34.10 μg/l.

When increased water volumes (880 ml) were preconcentrated, the recovery decreased to 50–57%. In previous papers when preconcentrating endosulfan [27] and eight organochlorine pesticides [28] on C_{18} disks low recoveries for 1-l water volume were observed (from 66 to 48%). Such low recoveries were attributed to the sorption of nanograms of analyte on the walls of laboratory glassware when using large water volumes. At these volumes, when

Table 1
Recovery of α-, β- and endosulfan sulphate using C_{18} Empore disks at different water volumes, each experiment with $n=3$

α				β				Sulphate			
Conc. (μg/l)	Volume (ml)	Recovery (%)	R.S.D.	Conc. (μg/l)	Volume (ml)	Recovery (%)	R.S.D.	Conc. (μg/l)	Volume (ml)	Recovery (%)	R.S.D.
17.36	25	88.28	16.25	17.05	25	84.54	10.45	13.88	25	57.01	11.65
17.36	100	88.92	15.32	17.05	100	81.28	9.39	13.88	100	45.91	17.96
17.36	250	66.63	4.00	17.05	250	71.30	2.82	13.88	250	44.19	10.62
17.36	800	51.34	3.59	17.05	800	47.04	3.32	13.88	800	39.80	4.23
34.72	25	72.97	4.53	34.10	25	84.02	29.69	27.76	25	50.07	13.53
34.72	50	84.95	10.44	34.10	50	78.06	15.06	27.76	50	62.35	12.55
34.72	100	70.18	4.65	34.10	100	71.61	5.07	27.76	100	51.77	10.78
34.72	250	62.80	8.76	34.10	250	72.62	10.33	27.76	250	50.37	8.21
34.72	800	57.58	6.57	34.10	800	51.76	8.48	27.76	800	50.37	8.21

R.S.D., relative standard deviation.

the glassware surface is in contact with the pesticide and since organochlorines exhibit a high octanol–water partition coefficient (log K_{ow} value) (the endosulfan is close to 5), organochlorine pesticides can remain on the glassware walls. This can be avoided by using completely silanized glassware. The recovery values at 800 ml of water are indicated since this was the volume used in monitoring ground water samples in Almeria.

3.2. Stability on C_{18} empore disks

The different disks spiked with α- and β-endosulfan were analyzed during a 3-month period (Table 2). When removed from storage at −20°C and 4°C the disks were kept at room temperature for 15 min before elution with ethyl acetate (3×10 ml). We used the half concentration of photodegradation experiments and a volume of 50 ml in the preconcentration.

Endosulfan was found to be stable in Empore disks for a period of 3 months and at three different temperatures. Since the monitoring took place 1000 km from the laboratory, the storage of samples into disks does not represent any problem and disks can be used instead of water bottles.

3.3. Photodegradation kinetic of α- and β-endosulfan

All photodegradation reactions determined in this work were of first order. The photolysis of endosulfan in deionized water with sunlight showed 46.59% degradation for α-isomer and 42.89% for β-isomer, during 384 h of solar irradiation (Table 3). The half-life was shorter than from other studies, since photolysis took place during August. A half-life of 183.4 days at pH 7.0 and 30°C was reported in a study of the influence of pH and temperature in degradation of endosulfan [15]. Our study indicated that endosulfan is degraded quickly when solar irradiation or extreme pH and high temperatures are used. Ferrando et al. [16] used a 20-l glass aquarium (UV transmittance), well-aerated with compressors, with sunlight and determined a half-life of 50.31 h in natural water and 67.83 h in experimental water (tap water of Valencia, Spain). The increase of degradation noticed by Ferrando was mainly due to aeration. In addition, irradiation from Valencia sunlight is more close to equatorial line, compared with Barcelona. Therefore faster degradation is expected.

The degradation with sunlight was increased when $FeCl_3/H_2O_2$, Fenton's reagent was added because ·OH radicals with high oxidation power are pro-

Table 2
Mean concentrations found in the study of stability of α- and β-endosulfan on C_{18} Empore disks

Temp. (°C)	Time (month)	α		β	
		Conc. (μg/l)	R.S.D. (%)	Conc. (μg/l)	R.S.D. (%)
−20	0	14.55	0.21	12.40	10.84
−20	1	14.25	4.47	11.36	3.66
−20	2	15.78	5.95	12.51	6.61
−20	3	14.07	14.59	12.70	12.56
0	0	14.55	0.21	12.40	10.84
0	1	16.46	11.62	12.69	6.60
0	2	18. 27	8.56	14.75	8.31
0	3	14.97	12.74	14.03	6.64
20	0	14.55	0.21	12.40	10.84
20	1	18.64	5.96	13.48	7.55
20	2	17.11	2.07	14.59	1.62
20	3	15.58	11.49	13.99	10.10

R.S.D., relative standard deviation.
Volume of water preconcentrated: 50 ml, spiked at 17.36 μg/l for α-endosulfan and 17.05 μg/l for β- endosulfan.

Table 3
Percentage of degradation of α- and β-endosulfan with sunlight in deionized water, using a initial concentration of 35 μg/l of each isomer

Without $FeCl_3$			With $FeCl_3$		
Time (h)	α Degrad. (%)(S.D.)	β Degrad. (%)(S.D.)	Time (min)	α Degrad. (%)(S.D.)	β Degrad. (%)(S.D.)
0	0.00	0.00	0	0.00	0.00
48	6.03 (2.29)	11.12 (1.00)	8	18.35 (10.16)	22.18 (7.69)
96	7.71 (1.79)	17.48 (0.05)	16	25.57 (11.70)	36.08 (3.62)
144	9.24 (1.06)	21.23 (1.18)	24	38.67 (10.16)	33.79 (6.75)
192	10.57 (1.99)	23.06 (1.98)	32	39.96 (8.10)	34.39 (7.40)
240	18.00 (1.04)	24.72 (1.33)	40	41.98 (14.36)	37.13 (2.28)
288	21.91 (1.21)	24.89 (1.14)	48	56.73 (6.84)	41.75 (7.89)
336	37.39 (0.71)	31.17 (0.80)	56	52.06 (3.54)	42.64 (4.58)
384	46.59 (0.91)	42.89 (0.91)	64	53.46 (4.59)	45.53 (9.87)
			72	62.07 (1.22)	55.52 (0.97)

Number of experiments, for each degradation experiment, $n=3$.
S.D., standard deviation.

duced. The degradation was 62.07% for α-endosulfan and 55.52% for β-endosulfan, for 72 min (Table 3).

The degradation of both isomers with xenon arc lamp was faster than with sunlight. α-Isomer in deionized water with xenon arc lamp degraded 57.71% at 96 h (Table 4) and with sunlight degraded 7.71% at 98 h (Table 3). β-Isomer in deionized water with xenon arc lamp degraded 70.30% at 96 h and with sunlight degraded 17.48% at 98 h. This was expected, since the UV emission contribution is more significant using xenon lamp and the irradiance is between 5 and 10 times higher according to the wavelength with xenon arc lamp than with sunlight, according to the light intensity measured in previous work [23].

In ground water, the degradation was faster than in deionized water (Table 4). We have determined for α-isomer a half-life of 79 h and 25 h in deionized water and in ground water, respectively (Table 5), and for β-isomer a half-life of 54 h and 18 h in deionized water and in ground water, respectively

Table 4
Percentage of degradation of α- and β-endosulfan with xenon arc lamp, using a initial concentration of 35 μg/l of each isomer

Time (h)	Deionized water		Ground water	
	α Degrad. (%)(S.D.)	β Degrad. (%)(S.D.)	α Degrad. (%)(S.D.)	β Degrad. (%)(S.D.)
0	0.00	0.00	0.00	0.00
6	7.49 (2.37)	12.76 (11.06)		
12	14.96 (3.30)	15.82 (8.57)	37.69 (2.40)	41.91 (4.46)
18	15.87 (0.80)	22.35 (9.29)		
24	20.96 (11.05)	34.25 (4.77)	61.55 (3.79)	83.75 (1.27)
36	32.86 (13.36)	45.55 (10.80)	71.38 (1.27)	89.97 (0.51)
48	39.24 (4.17)	54.94 (3.30)	80.85 (0.50)	94.61 (1.37)
60	44.02 (6.63)	57.56 (7.03)	82.41 (1.15)	94.54 (3.63)
72	44.90 (6.69)	60.58 (5.50)	87.17 (0.27)	96.41 (1.23)
84	54.33 (7.98)	68.94 (3.74)	91.01 (1.70)	97.17 (0.55)
96	57.71 (2.52)	70.30 (0.21)	93.99 (0.36)	97.51 (1.21)

Number of experiments, for each degradation experiment, $n=3$.
S.D., standard deviation.

Table 5
Kinetic of α-endosulfan photodegradation in water

Photodegradation	Reaction order	Rate constant (1/time)	R.S.D.	Half-life
Sunlight, deionized water	1	0.0014	17.0	479 h
Xenon lamp, deionized water	1	0.0087	4.0	79 h
Xenon lamp, ground water	1	0.0274	4.7	25 h
Xenon lamp, deionized water, $FeCl_3$	1	0.0070	12.6	99 min
Xenon lamp, deionized water, TiO_2	1	0.0072	7.6	97 min
Sunlight, deionized water, $FeCl_3$	1	0.0121	9.9	57 min

Number of experiments, for each degradation experiment, $n=3$.
R.S.D., relative standard deviation.

(Table 6). Rates of photodegradation can be affected by dissolved and suspended matter in aqueous media [29]. For example, rates of photoreaction can be affected by the absorption or scattering of light in aqueous media via physical processes or by photochemical processes involving sensitization or quenching of excited states [29]. Moreover, the role of some inorganic anions such as nitrate in inducing photoxidation of organic compounds in water was verified [29].

The photodegradation of α- and β-endosulfan in deionized water was very fast using xenon arc lamp, and $FeCl_3/H_2O_2$ and TiO_2/H_2O_2, respectively. At 250 min, α-isomer was degraded 86.43% with TiO_2/H_2O_2 (Table 7) and β-isomer was degraded 87.53% with TiO_2/H_2O_2, and 86.05% with $FeCl_3/H_2O_2$ for α-isomer (Table 7) and 86.80% with $FeCl_3/H_2O_2$ for β-isomer. Dureja et al. [12] used triethylamine to induce the photolysis of endosulfan and determined a half-life of 1.3 h for α-isomer and 1.8 h for β-isomer when the irradiation was done with sunlight. We determined a half-life of 99 min for α-isomer and 79 min for β-isomer when the photocatalysis was done with $FeCl_3$ and xenon arc lamp, and 97 min for α-isomer and 99 min for β-isomer when the photocatalysis was done with TiO_2 and xenon arc lamp, and 57 min for α-isomer and 85 min for β-isomer when the photocatalysis was done with $FeCl_3$ and sunlight. Therefore, using TiO_2 or $FeCl_3$ enhanced the degradation of endosulfan in water.

It is interesting to notice that endosulfan degrade very fast without artificial irradiation when TiO_2 or $FeCl_3$ is added. $FeCl_3$ has been used in waste-water treatment plants, and for these reasons, the $FeCl_3/H_2O_2$ system and sunlight is very favorable to destroy contaminants in waste-water. The catalytic ability of TiO_2 to generate hydroxyl radicals that degrade organic contaminants in aqueous systems has led to several papers about photocatalysis with this semiconductor, and good results were reported [30], Bolton and Sun [31] found that when using TiO_2 suspensions only about 4% of the absorbed photons actually produce hydroxyl radicals. However, when TiO_2 is used with H_2O_2, the catalytic power is increased. We have found that pesticides (alachlor, chlorpyrifos and endosulfan) degrade very fast when TiO_2/H_2O_2 system is used.

A groundwater sample taken from monitoring point (D_1) was irradiated by photolysis with xenon arc lamp and photocatalysis with $FeCl_3$ and xenon

Table 6
Kinetic of β-endosulfan photodegradation in water

Photodegradation	Reaction order	Rate constant (1/time)	R.S.D.	Half-life
Sunlight, deionized water	1	0.0011	13.3	615 h
Xenon lamp, deionized water	1	0.0128	5.1	54 h
Xenon lamp, ground water	1	0.0382	12.5	18 h
Xenon lamp, deionized water, $FeCl_3$	1	0.0088	10.0	79 min
Xenon lamp, deionized water, TiO_2	1	0.0070	7.3	99 min
Sunlight, deionized water, $FeCl_3$	1	0.0082	15.6	85 min

Number of experiments, for each degradation experiment, $n=3$.
R.S.D., relative standard deviation.

Table 7
Percentage of degradation of α- and β-endosulfan in photocatalysis with xenon arc lamp

Time (min)	With TiO_2		With $FeCl_3$	
	α Degrad. (%)(S.D.)	β Degrad. (%)(S.D.)	α Degrad. (%)(S.D.)	β Degrad. (%)(S.D.)
0	0.00	0.00	0.00	0.00
10	17.23 (15.86)	19.77 (8.92)	16.72 (17.60)	13.13 (16.81)
15	25.07 (1.67)	28.99 (6.41)	21.65 (9.37)	18.25 (8.94)
20	38.09 (1.34)	35.89 (14.08)	44.59 (5.09)	28.84 (3.27)
30	46.34 (9.96)	51.04 (2.01)	53.70 (11.15)	39.24 (24.01)
40	50.94 (5.87)	49.86 (4.84)	57.59 (10.34)	44.49 (5.92)
50	52.36 (15.70)	52.74 (10.96)	60.26 (18.64)	52.16 (18.06)
60	59.84 (3.91)	55.68 (11.33)	67.19 (1.69)	59.88 (3.72)
70	63.39 (10.43)	60.89 (7.16)	66.54 (19.11)	75.17 (25.07)
90	60.39 (3.96)	55.77 (13.57)	72.15 (14.39)	65.33 (6.19)
110	68.71 (0.53)	63.31 (11.50)	73.23 (11.65)	67.16 (13.32)
130	66.01 (4.23)	65.88 (9.73)	74.42 (11.86)	69.64 (11.08)
160	74.08 (4.28)	73.38 (5.63)	68.33 (5.86)	76.83 (9.79)
200	83.11 (1.35)	80.93 (8.90)	85.46 (4.74)	91.19 (4.27)
250	86.43 (1.74)	87.53 (5.10)	86.05 (18.90)	86.80 (3.689

Number of experiments, for each degradation experiment, $n=3$.
S.D., standard deviation.

arc lamp (Table 8). α-Endosulfan was degraded 85.6% at 96 h of photolysis and 77.2% at 5 h of photocatalysis with $FeCl_3$, and β-endosulfan was degraded 91.4% at 96 h of photolysis and 81.7% at 5 h of photocatalysis with $FeCl_3$. With a real sample, the $FeCl_3/H_2O_2$ system showed the photocatalytic power of oxidation.

In the photolysis with sunlight, the half-life for α-endosulfan was shorter than β-endosulfan, and in the photocatalysis with $FeCl_3$ and in the photolysis with xenon arc lamp, the half-life for the β-isomer is shorter than for the α-isomer. In the photocatalysis with TiO_2 the half-life is similar for both isomers.

Different results on the degradation rate of α- and β-endosulfan depending of experimental conditions were reported. α-Endosulfan has exhibited a half-life shorter or longer than β-endosulfan [1,12,14,20].

3.4. Degradation products

Endosulfan sulphate was detected as degradation product by GC–MS in a few samples. It was difficult to detect endosulfan sulphate because of its low concentration and low response factor. The low recovery of endosulfan sulphate (Table 1) did not permit a larger amount of metabolite to be analyzed by GC–MS and GC–ECD.

Other degradation products were reported as endosulfan diol, endosulfan ether, endosulfan lactone, endosulfan hydroxyether and endosulfan dialdehyde

Table 8
Percentage of photodegradation of endosulfan in an Almeria ground water sample, using a xenon arc lamp

	α		β	
	Conc. (ng/l)	Degrad. (%)	Conc. (ng/l)	Degrad. (%)
Without photodegradation	2.57	0	10.40	0
Photolysis, 96 h	0.37	85.6	0.90	91.3
Photocatalysis $FeCl_3$, 5 h	0.59	77.2	1.89	81.8

but were not detected. Kullman and Matsumura [32] identified these metabolites when *Phanerochaete chrysosporium* was used for degradation of endosulfan. Akther and Siddiqui [33] found the metabolites sulphate, diol, ether and lactone when degraded endosulfan by soil microorganisms. Cotham and Bidleman [14] found one metabolite, endosulfandiol, when samples of seawater and seawater/sediment microcosms were incubated in flasks at 20°C, under laboratory light.

Endosulfan sulphate was formed in all our reactions of photodegradation. Some of the others metabolites may also have been formed but were not detected because of their low recovery or/and its high polarity or/and they were produced in very low concentrations. Since low concentrations of endosulfan were used for the study of photodegradation then the others metabolites were not detected.

Fig. 1 shows a chromatogram of GC–ECD, a chromatogram of GC–MS and the spectrum of endosulfan sulphate. The sample did not need a high preconcentration in the analysis by GC–ECD to detect endosulfan sulphate but the GC–MS analysis needed a high preconcentration (600 times).

3.5. Monitoring of ground water

The monitoring of pesticides in grounds waters of Almeria, was done during 1 year. Almeria has 36 400 hectares of cultivated fields (mainly greenhouses), this region has become one of the major suppliers of green vegetables to most of the EU countries. The major crops cultivated include peppers, tomatoes, melons and cucumbers [23]. In this work, we report the results of monitoring of α-, β- and endosulfan sulphate that were obtained in our laboratory.

We found α-, β- and endosulfan sulphate in the majority of sampling points (Tables 9–11) and several of the results show high contamination, as in D1 and CN8. The major concentrations occurred between September and December following application of pesticides. Large amounts of insecticides, and to a lesser extent fungicides, are sprayed to improved crop yields [23]. This pesticides are being used for cultivation of a variety of crops. Endosulfan is used because it is very effective on crops such as onions, green peach, corn, soybean, peppers, apples, etc. [7]. Moreover, under field conditions plants are more tolerant to endosulfan than other insecticides and residues of endosulfan on plant surfaces are less persistent than in water [7]. One of the major factors affecting leaching is the water recharge rate (rainfall plus irrigation minus evapotranspiration). Extensive use of irrigation has been one of the reasons for the movement of agrochemicals in the soil. Since high irrigation takes place during summer period (June–July) due to the high temperatures, this favors the leaching of pesticides to the ground water, similarly as observed for carbamates. For this reason, higher concentrations of endosulfan are found between September and December, following application and irrigation. It should be noticed that concentrations of endosulfan sulphate are higher than of endosulfan almost during all the year with the exception of September, October and November, following fresh application of endosulfan and leaching to the ground water.

The sample of monitoring that we used for photodegradation, corresponded to one of the more contaminated places (D1), but it was taken in April of 1997 when the contamination had diminished. However, it was showed that photocatalysis and photolysis degraded endosulfan.

4. Conclusions

The extraction with C_{18} Empore disks in photodegradation studies permits the study of degradation of endosulfan-isomers at lower concentrations. GC–ECD and GC–MS can be used to characterize the different samples.

Endosulfan isomers were degraded slowly using natural or artificial irradiation, but were degraded very fast with photocatalysis using the $FeCl_3/H_2O_2$ or TiO_2/H_2O_2 systems. Using $FeCl_3/H_2O_2$ the degradation of endosulfan isomers was very fast in ground water. This system has shown that using only 15 mg/l of $FeCl_3$, it is a very effective method for the destruction of endosulfan in waters.

We have identified one degradation product of endosulfan-isomers, endosulfan sulphate. The α- and β-endosulfan compounds were stable on C_{18} Empore disks at −20°C, 4°C and 20°C.

The degradation was performed at the concen-

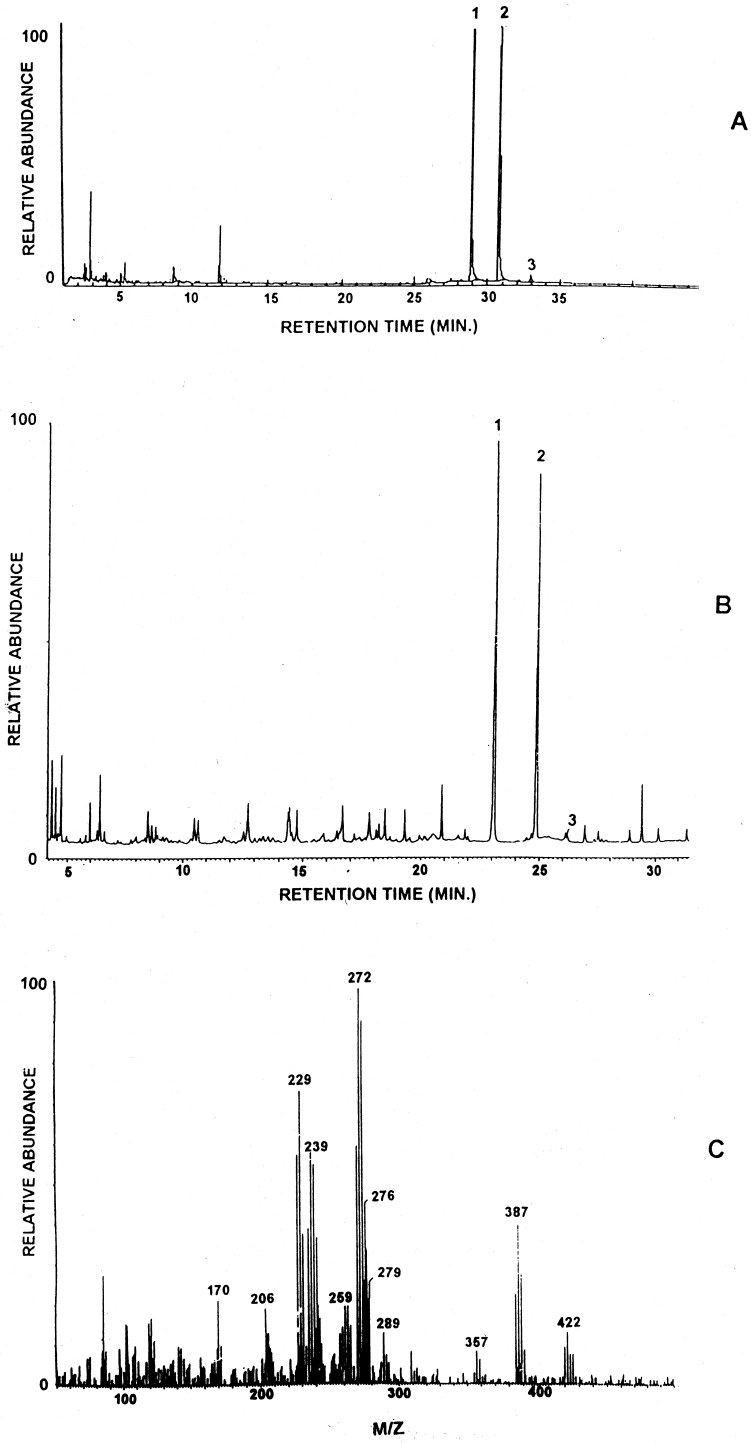

Fig. 1. (A) GC–ECD chromatogram of a preconcentrated water sample (25 times) of the photodegradation experiments (photolysis with xenon arc lamp, 72 h). Peaks 1, 2 and 3 correspond at α-, β- and endosulfan sulphate, respectively. (B) GC–MS chromatogram of a preconcentrated sample (600 times) of the photodegradation experiments (photolysis with xenon arc lamp, 72 h). Peaks 1, 2 and 3 correspond at α-, β- and endosulfan sulphate, respectively. (C) MS spectra (scan mode) of endosulfan sulphate in the sample (B).

Table 9
Monitoring of α-endosulfan in ground water samples of Almeria

Sampling points	D1	D2	D3	CN1	CN5	CN7	CN8	CN9
April 1996	8.90				15.48			
May 1996	8.82		2.52	4.36		21.30		
June 1996	6.06	0.70	0.66	0.54	1.66			
July 1996	2.46		1.92	1.12	3.94	8.46		
September 1996	104.84	3.56	22.72	3.92				
October 1996	51.94	12.78	6.54	7.16				
November 1996	45.86	6.06	3.18	69.76			447.49	30.54
December 1996	21.72	1.10	0.80	2.50			39.00	
January 1997	6.10	1.06	0.56					22.08
February 1997	1.76	0.90	3.02	7.98			13.36	
March 1997	16.14	0.52	6.58					

Concentrations expressed in ng/l.
All values are corrected by recovery at 800 ml.

Table 10
Monitoring of β-endosulfan in ground water samples of Almeria

Sampling points	D1	D2	D3	CN1	CN5	CN7	CN8	CN9
April 1996	38.92				7.48			
May 1996	16.64		1.50	20.14		18.04		
June 1996	20.32	0.98	1.02	0.76	0.82			
July 1996	5.98		1.14	0.66	3.04	5.70		
September 1996	247.78	3.14	36.76	1.64				
October 1996	376.14	8.58	11.86	3.30				
November 1996	211.42	21.48	8.00	85.18			338.94	130.92
December 1996	101.48	3.34	2.16	2.34			37.74	
January 1997	26.50	9.82	0.94					25.94
February 1997	18.20	2.32	1.58	3.06			25.72	
March 1997	54.18	1.28	1.12					

Concentrations expressed in ng/l.
All values are corrected by recovery at 800 ml.

Table 11
Monitoring of endosulfan sulphate in ground water samples of Almeria

Sampling points	D1	D2	D3	CN1	CN5	CN7	CN8	CN9
April 1996	85.42				n.d.			
May 1996	71.28		6.22	12.42		n.d.		
June 1996	45.32	n.d.	n.d.	5.70	10.62			
July 1996	42.56		8.66	n.d.	n.d.	2.18		
September 1996	188.34	7.30	35.98	6.20				
October 1996	292.24	190.56	61.34	18.20				
November 1996	97.36	1.54	1.38	12.62			359.06	190.58
December 1996	125.48	3.68	3.76	0.98			539.48	
January 1997	24.86	21.56	1.76					7.78
February 1997	16.60	5.40	4.40	65.36			367.54	
March 1997	20.76	n.d.	n.d.					

Concentrations expressed in ng/l.
All values are corrected by recovery at 800 ml.

tration levels of endosulfan-isomers close to environmental conditions (μg/l) so the results obtained in this work can be used to predict its behavior in real environmental situations.

A monitoring in Almeria showed that significant amounts of endosulfan are detected in ground waters, and indicated that the use of C_{18} disks is a good alternative for analysis and storage of endosulfan in water.

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